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Review on the titanium oxide for catalytic applications

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Abstract: Titanium dioxide (TiO_2) presents particular importance, due to its general properties in a wide range of fields, such as catalysis, photocatalysis and antibacterial agents and as nano-paint (self-cleaning). Physical and chemical characteristics of TiO_2, particle size and shape, phases of crystalline TiO_2 with band gaps that rutile TiO_2 of 3.0 eV and anatase TiO_2 of 3.2 eV, determine the photocatalytic performance of TiO_2. This review presents the theoretical concepts of the structure properties of this oxide and the elaboration methods that make TiO_2 the ideal candidate for catalytic applications.

Keywords: titanium oxide,rutil, anatase, properties, morphologies, elaboration

1. Introduction

Titanium oxide (TiO_2) is one of the most studied inorganic compounds in chemistry; because it is an alkaline oxide whose synthesis, physical and chemical properties, and uses have been the subject of numerous studies, for all its crystallographic forms (anatase - A, rutile - R and brookite - B).

Titanium oxide TiO_2 is a material of great interest due to the chemical, physical, optical and electronic properties that make this material a reference in several catalytic applications. Its properties depend on the crystal, structure, size of the particle that influences the surface.

A large number of applications, such as air and water treatment, self-cleaning surfaces, electronic devices and solar cells, have been reported in the literature [1-8]. Recently, Fujishima and his colleagues have highlighted the large number of publications on this metal oxide with catalytic applications [9]. Numerous articles address on the topic of TiO_2 perspectives from the point of view of: heterogeneous photochemistry, photochemistry interspersed with the chemistry, physics and engineering of this material. There are also reviews that address the role of TiO_2-based materials in areas such as photo catalytic splitting of water and obtaining hydrogen, photo electrochemistry, dye sensitization and conversion of solar energy, designing reactors and kinetic processes, as well as photochemical treatments of air and water [10-12].

2. Structure and properties

Titanium oxide occurs naturally in three crystalline structures: rutile, anatase and brookites. All three structures are composed of a TiO_6 octahedron linked in different ways.

The TiO_2 structure consists of TiO_6 octahedral chains, where each Ti atom is surrounded by 6 oxygen

atoms. The unit cell of the tetragonal anatase contains four units TiO_2 (12 atoms), while the unit cell of the tetragonal rutile contains two units TiO_2 (6 atoms), and the unit cell of the orthorombic brook contains eight units TiO_2 (24 atoms).
Thus, anatase has a smaller cell volume than that of rutile and brookite. Therefore, most scientific work was done with anatase or rutile. Brookit is the least stable phase of the three structures, due to the orthorhombic structure, so it is difficult to elaborate [13]. Figure 1. and 2 show the TiO_6 structure and the crystalline TiO_2 structures: rutile, anatase and brookites.

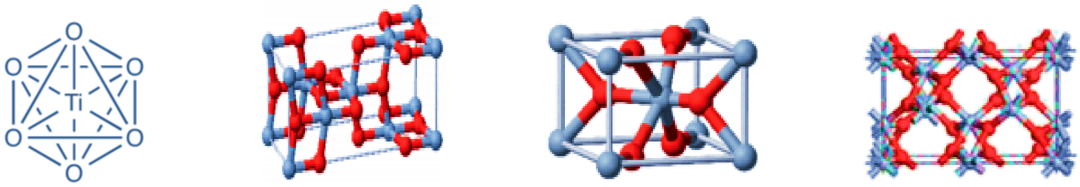

Figure 1.
a) TiO_6 structure b) Anatas (tetragonal structure) c) Rutile (simple tetragonal structure) d) Brookit (orthorhombic) [13, 14]

Each structure has different physical properties. Of these, rutile is the most stable phase under environmental conditions, while anatase and brookite are metastable and will become rutile when heated. Some studies have reported that the stability of the different TiO_2 phases depends on the particle size. Anatase is the most thermodynamically stable phase when nanoparticles are smaller than 11 nm, and rutile has been shown to be the most stable for nanoparticles larger than 35 nm [14]. The anatase phase of TiO_2 is known for its applications in photo catalysis, gas sensor, solar cells and electrochemical systems. The rutile phase of TiO_2 (simple tetragonal) has applications in the construction of electric capacitors, filters, power circuits and capacitors due to its high dielectric constant [15]. TiO_2 has been extensively studied in various photo catalytic systems, including photodegradation of volatile organic compounds, hydrogen production and other environmental applications due to its n-type semiconductor properties, with a range of 3.0 to 3.2 eV (depending on crystallographic variants), low toxicity potential, good chemical and thermal stability, surface acidity and selectivity [16-19]. The properties and applications of titanium oxide are summarized in Table 1.

Table 1. Examples of properties and applications of titanium oxide

TiO_2-phase	Color	Properties	Applications
Anatase - TiO_2	Brown to black	Polymorphic, metastable, lower absorption rate, high density, higher gap	Paints, papers, ceramics, solar cells, photocatalysis, etc
Rutil - TiO_2	Dark red	High refractive index, hard, chemically resistant, UV absorbent, obtained at high temperature	Paints, paper, plastic, food, sunscreen, photocatalysis, interference applications
Brookite - TiO_2	Dark brown to blackish green	Fragile, very rarely metastable polymorph, non-fluorescent	Photocatalysis, photovoltaic devices, jewelry

The structure dimension of TiO_2 has an impact on its properties and on the photocatalytic activity [20-21].In Figure 2, types of titanium oxide morphologies are presented based on its size.
Different methods of titanium dioxide elaboration, including hydrothermal methods and sol-gel processes using a variety of precursors such as titanium alkoxides, titanium tetrachloride have been reported by Kobayashi and co-workers 2007, Adjimi and co-workers 2014, Elsellami and its collaborators 2017 [25-27].

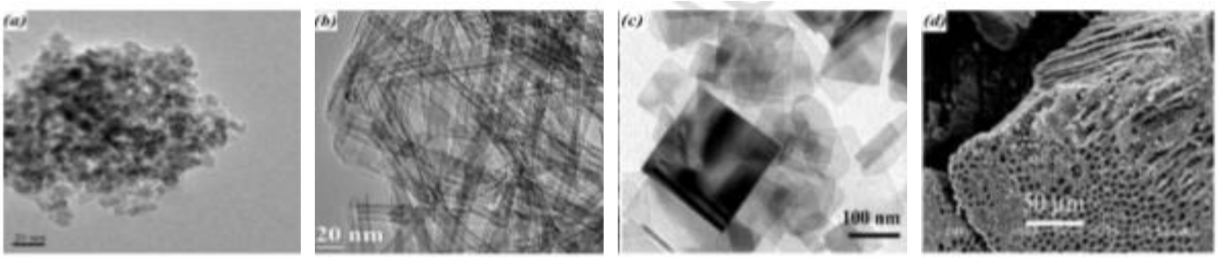

Figure 2. Examples of TiO_2 morphologies based on their size a) 0D- Nanoparticles [22], b) 1D- Nanotubes Nanofibers [23], c) 2D- Nanoplates [23] and d) 3D- Porous structures [24]

3. Methods of elaboration

3.1. Hydrothermal method

Hydrothermal method is an important method for elaboration mono-dispersed and homogeneous nanoparticles. By this method, nanoparticles, nanotubes, nanofibers, nanowires, nanoparticles and porous structures of titanium oxide were obtained from various precursors. The researchers in the field studied in detail the hydrothermal synthesis of TiO_2 particles, the influence of various parameters, such as temperature, experimental duration, pressure, solvent type and pH. The synthesis of TiO_2 is usually performed in small Morey type autoclaves fitted with teflon coatings. Depending on the solvent used, the synthesis procedure can generally be classified in two methods:

- the acid hydrothermal method consists of the use of the reactants: titanium salts and concentrated hydrochloric acid (HCl);
- alkaline hydrothermal method consists of the use of reagents: titanium salts and concentrated sodium hydroxide (NaOH).

These two methods have a different reaction mechanism, which produce different morphological characteristics of TiO_2.
Additional hydrothermal conditions such as precursor type, NaOH solvent concentration, temperature and reaction time can affect the structure and morphology of the nanostructures.
In the study by Chen and his colleagues, they developed titanium oxide (anatase, rutile and brookite) using as a precursor titanium butoxide by hydrothermal treatment in concentrated aqueous HNO_3 solution at 180°C for 24 hours. X-ray diffraction (XRD) results indicated that, as the acidity of the reaction medium was decreased, the content of anatase and rutile increased and decreased, while brookite formation was not affected. At the same time, the degree of crystallinity, crystal size and pore size decreased and the specific surface area was improved [31].
Similar relationships between phase content and acidity were also found by other researchers during the hydrothermal treatment of titanium oxide in ethanol-water solution.
Recently, Cano-Casanova and his colleagues conducted a detailed study on the crystalline structure of TiO_2 photocatalysts, elaborated by this method using TIP and HCl (0.5-12 M) titanium isopropoxide precursor. The HCl concentration had a major impact on the phase and size of the crystal. As the HCl concentration increased to 3 M, the phase content of anatase decreased, while the content of rutile and brookite increased steadily. At higher concentrations of HCl, the percentage of anatase increased with acidity of the solution and the content of rutile and brookite naturally decreased [32].Yu and his colleagues evaluated the rate of formaldehyde degradation under visible light over reduced graphene oxide (rGO) with TiO_2, elaborated by the hydrothermal reaction between TBOT and graphite powder [33]. Table 2 summarizes the morphologies of titanium oxide, the precursors used, the method of elaboration and characterization.

Tabel 2. Morphologies of titanium oxide, precursors, reaction parameters in the hydrothermal method

Precursors	Hydrolysis agent	Parameters T(°C) t(h)	Morphology	Characterization method	Crystal Phase	BET (m^2/g)	Dim. crystal	Ref. bibl.
Titanium butoxide	NaOH HNO_3	180°C 24 h		XRD	A+R+B	92-137	7.5-23	[31]
Titanium	EtOH, H_2O	180°C		XRD,	A+B,	100-	8-24	[32]

Precursors	Hydrolysis agent	Parameters T(°C) t(h)	Morphology	Characterization method	Crystal Phase	BET (m^2/g)	Dim. crystal	Ref. bibl.
isopropoxide	HCl	12 h	nanoparticles spherical	SEM,	A+B+R	135		
Titanium butoxide	Graphite powder; H_2SO_4; $KMnO_4$; H_2O_2; HCl; $NaNO_3$	180°C 12 h		XRD, TEM, XPS, Raman spectroscopy; UV-vis	A	62,5-100	-	[33]

3.2. SOL-GEL Method

Sol-gel is represented by the process of hydrolysis of the alkoxides is the most used method of elaboration of TiO_2 with photocatalytic properties, since the equipments and precursors necessary for the elaboration of the method are cheap. TiO_2 nanopowders can be obtained by hydrolysis of titanium alkoxides. The process parameters influence the properties of the resulting products. Of these I mention:

- concentration of reactants;
- pH of the solution;
- the temperature at which the hydrolysis process takes place;
- the nature of catalysts.

The general reaction equation of the process is:

$$Ti(OR)n + H_2O \rightarrow TiO_2 + R\text{-}OH$$

If titanium tert-isopropoxide is used, the chemical reaction is as follows:

$$Ti(CH_3\text{-}CH_2\text{-}CH_2\text{-}OH)_4 + 2H_2O \rightarrow TiO_2 + 4CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$$

In the case of titanium butoxide, the chemical reaction is as follows:

$$Ti(CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH)_4 + 2H_2O \rightarrow TiO_2 + 4CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$$

O. Kaygili et all. used titanium tetra-isopropoxide precursor in ethyl alcohol to which 100 ml of distilled water was added. The obtained solution was stirred continuously for 10 minutes to obtain the gel. Thereafter, it was stirred without heating for 2h30 min in a magnetic stirrer. This was introduced into an oven, maintained at 60 ° C for 24 hours and further dried at 800C for 22 hours. Omer calcined the gel obtained at 11000C for 2h to form white TiO_2 powder [34]. BK. Mutuma et all used titanium tetra-isopropoxide as precursor to which 30 ml of isopropyl alcohol was added and stirred for 20 min. Deionized water (300 ml) was added to the mixture under vigorous stirring. The solution was heated to 80°C for 5 hours and then cooled to room temperature. After cooling, the pH of the solution was controlled by the addition of 1M NaOH or 1M HNO_3 to obtain soils at pH 2, 4, 7 and 9. The soils were allowed to gel at room temperature (25°C) for 24 hours. h. The obtained gels were filtered, washed with distilled water and then rinsed with ethanol and dried at 100° C for 12 h. The samples were calcinated at 200°C, 600°C and 800°C for 2 h. In this work BK. Mutuma highlights the formation of TiO2 nanoparticles with anatase - brookite using pH control [35]. Unlike O. Kaygili and BK. Mutuma, N.Varghese et all. used tetra-isopropoxide precursor titanium, 2-propanol and deionized water in molar ratio of 1: 2: 12. After stirring the solution, gelatin and nitric acid were added. The SEM and XRD results demonstrate that the use of gelatin in the sol-gel method of titanium oxide nanoparticles - rutile phase, improves crystallinity and decreases the particle size, so with and without gelatin, the particle size was 40 nm and 20 nm respectively [36]. By this method TiO_2 films can be obtained on different substrates.

Thus, M. Vishwas and his colleagues and T. Rattana and collaborators obtained TiO_2 films on different substrates. For example, M. Vishwas and his colleagues used ITO-coated glass substrate dissolved 10 ml of titanium isopropoxide in 100 ml of ethyl alcohol (99.8%). After the addition of concentrated HCl, the solution was stirred for up to half an hour. The clear solution was obtained which was kept in a sealed beaker for two hours for gel formation. The solutions were centrifuged on

the glass substrate to obtain films. Then, the films were preheated to 60 ° C for 6 hours and then annealed at different temperatures 200 ° C, 250 ° C and 300 ° C for 6 hours [37].
T. Rattana et al. Obtained TiO_2 films on silicon plate substrate, stainless steel, and glass sheet. Thus, 100 ml of 0.2 M titanium tetra-isopropoxide was added to isopropanol under continuous stirring. Add small amounts of deionized water to the precursor solution. The solution was stirred for 10 min before nitric acid was added to adjust the pH to 2. The precursor solution was further stirred at room temperature for 1 hour until the homogeneous solution was obtained. The precursor solution was coated on a glass blade, stainless steel and silicon plate. The prepared films were dried at 90 ° C in air for 10 minutes to remove an organic solvent from the films. Finally, the dried films were annealed at 550°C for 1 h [38]. Recent literature reveals that the sol-gel method has proven to be an efficient and versatile method for making TiO_2 powders and films.
Table 3 shows the morphologies of titanium oxide, precursors, reaction parameters, method of elaboration and characterization.

Table 3. Morphologies of titanium oxide, precursors, reaction parameters in the sol-gel method

Precursors	Hydrolysis agent	Parameters T(°C) t(h)	Morphology	Characterization method	Crystal Phase	BET m^2/g	Dim crystal
Titanium butoxide $Ti(OBu)_4$	EtOH H_2O	60°C 24 h 80°C 22h	nanopowders, nanoparticles	XRD, EDX	R	23,21-27,51	[34]
Titanium tetra-isopropoxide	Isopropyl alcohol NaOH	80°C 5h		XRD, SEM,	A+B	-	[35]
titanium tetra-isopropoxide	Propanol H_2O	1000°C 2h		XRD, SEM	R	35-40	[36]
Titanium isopropoxide	Ethyl alcohol HCl	60°C 6h	filme	XRD, AFM	A	-	[37]
titanium tetra-isopropoxide	Isopropanol HNO_3	25°C 1h		AFM Raman	A	-	[38]

3.3. Precipitation method

This method is based on the hydrolysis of the precursors with hydrolysis agents that allow homogenization at the molecular level. By this method, TiO_2 nanoparticles were developed.
Namin and his colleagues obtained titanium dioxide nanoparticles by precipitating aqueous solution of TiCl4 with ammonium hydroxide as the precipitating agent. The prepared gel was allowed to crystallize for 6 h above 9°C, then dried at 100°C. Powder X-ray diffraction studies indicate the formation of anatase TiO_2 phase with an average crystal size of 4.5 nm [39].
Research conducted by W. Buraso and co-workers mentions obtaining titanium dioxide nanoparticles by a simple precipitation method using titanium isopropoxide (IV) as a precursor. The precursor powder was calcinated in air at temperatures between 400°C and 700°C. The results of the XRD analysis revealed that the size of the crystallite and the crystallinity of the samples increased with increasing calcination temperature. The calcination temperature had a significant influence on the average particle size, as the size increased from 11.3 to 27.4 nm when the temperature was raised from 400° C to 700° C [40].
J. Morales and his collaborators obtained TiO_2 nanoparticles, an anatase phase with an average crystallite size of around 20 nm, using the co-precipitation method using titanium butoxide as a precursor. It mixed titanium butoxide, ethanol, glacial acetic acid and sulfuric acid to obtain a white precipitate. The preparation of the starting solution was performed under magnetic stirring and heated to 55°C. The solution was centrifuged at 3500 rpm for 30 min. The powder was dried at 100°C for 2 hours and then calcinated at different temperatures (450°C, 550°C, 600°C, 650°C) and at different times (6, 12 and 24 h). According to the structural and morphological characterization, powders calcinated at 650 °C for 6 hours can be selected as the best to be used in gas detection applications, due to the quality of the anatase phase and the particle size [41].

Table 4 shows the titanium oxide morphologies obtained from different precipitating precursors and the morpho-structural characterization results.

Table 4. Morphology of titanium oxide, precursors, reaction parameters in the precipitation method

Precursors	Hydrolysis agent	Parameters T(°C) t(h)	Morphology	Characterization method	Crystal Phase	BET (m^2/g)	Dim crystal
$TiCl_4$	NH_4OH	90°C 6 h 80°C 22h	Nanoparticles	XRD,	A	4,5	[39]
titanium tetra-isopropoxide	H_2O	80°C 12h		XRD, SEM,	A R	10,2 47,3	[40]
Titanium butoxide (IV)	ethanol, glacial acetic acid and sulfuric acid	100°C 2h		XRD, SEM,TEM	A	18-22	[41]

3.4. Sonochemical method

The sonochemical approach was used in the synthesis of various nanostructured materials including high surface area colloids, alloys, oxides, carbides and transition metals. In recent years, research has focused on the development of TiO2 nanoparticles. Arami and his collaborators developed TiO_2 nanoparticles, the rutile phase with the average size of the 15nm crystallite, the diameter of 20 nm and the surface area of 78.88 m^2g^{-1} by the sonochemical method. They observed that aqueous NaOH broke the Ti-O-Ti bonds in the TiO_6 octahedron during the initial reaction and then new octahedra were developed after ultrasonic irradiation thus leading to nanostructured TiO_2 [42].

In the research conducted by A. Ibrahim and his collaborators, they successfully developed this method followed by calcination of TiO_2 nanopowders, anatse and rutile phase. They used titanium isopropoxide in 20 ml of ethanol and homogenized for 2 hours. The high intensity ultrasound probe (750 W 20 kHz) was immersed directly in the mixed solution at room temperature for 30 min. After the sonochemical process, the prepared precipitate was washed with deionized water and dried in the oven for 30 min. The white precipitates were calcined at different temperatures in the range of 400°C to 1000°C for 5 hours. The average crystallite size of TiO_2 powders at different calcination temperatures was in the range 12-96 nm. The increase of the crystallite size was influenced by the high calcination temperature [43].

In contrast to H. Arami and A. Ibrahim, S.Boini and his colleagues developed by sonochemical synthesis of TiO_2 nanoparticles with 50-100 nm dimensions starting from the tetraisopropoxide precursor titanium, ethanol and sodium hydroxide. The sonochemical process was performed at different amplitudes (50-100). The synthesized TiO2 nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM). This method not only helped reduce the size of the TiO_2 particles, but significantly reduced the crystal size of the nanoparticles [44].

Table 5 presents the morphologies of titanium oxide, precursors, method of elaboration and characterization.

Table 5. Morphologies of titanium oxide, precursors, reaction parameters in the method of sonochemical

Precursors	Hydrolysis agent	Parameters T(°C) t(h)	Morphology	Characteriza-tion method	Crystal Phase	BET (m^2/g)	Dim crystal
TiO_2 pellets	NaOH	40 kHz 350 W) 2 h 64°C 24h		SEM, XRD	R	15	[42]

Tetra-izopropoxid de titan	EtOH, deionized water	750 W 20 kHz 30min	Nanoparticles	XRD	A R	12-47 68-96	[43]
Tetra-izopropoxid de titan	NaOH, EtOH	50-100 Amplitude 1h		XRD, TEM	A	38	[44]

3.5. Microwave assisted method

This is a simple, biodegradable technique that ensures fast heating. This method allows the elaboration of small metal oxide nanoparticles with the desired crystallinity and good dispersibility.The method requires additional stabilizing agents, thus avoiding contamination of nanoparticles with intermediate products, which is extremely important for catalytic processes.

M. Guel et al elaborated with this TiO_2 method. He added a solution of 2 ml of titanium (IV) isopropoxide, 30 ml of 2-propanol and 2 ml of acetic acid or 3M hydrochloric acid in a Teflon vessel of microwave equipment. This equipment was programmed at a power of 400W at a temperature of 80°C. The obtained soil was kept at room temperature for 24 hours. Then, 8 ml of water was added to form a gel which was dried at 100 ° C for 24 hours. The gel was calcinated at 40 ° C for 3 hours. A single phase of anatase was formed after a reaction time of only 15 min, when acetic acid was used as a catalyst. This time period is considerably shorter than that required by the conventional sol-gel method. When hydrochloric acid was used as a catalyst, the three crystalline phases of TiO_2 were observed: anatase, rutile and brookite [45].

Ch. Ashok and his colleagues successfully developed TiO2 nanoparticles using this method, using titanium isopropoxide and NaOH. To the solution of titanium isopropoxide mixed with 50 ml of distilled water under stirring, 0.01M NaOH is added until the solution is white. This obtained solution is introduced in the microwave oven, for 5 minutes forming a white precipitate, finally obtained TiO2 particles of dimensions 18-21nm following the characterization by X-ray diffraction. The electron microscopy demonstrated the of spherical TiO2 nanoparticles [46].

In the research conducted by K.F Moura together with his collaborators, they described the method of elaborating TiO_2 with anatase structure using Ti (IV) isopropoxide and ethanol without alkalizing agents. They prepared an ethanol suspension using Ti (IV) isopropoxide and ethanol under continuous stirring. This suspension was heated by microwave radiation at 1200C at pressures of approximately 200 kPa, for reaction times of 1, 5, 15, 30 and 60 min. During the reaction, a white precipitate formed; after completion of the reaction, this precipitate was washed with distilled water at room temperature until complete neutralization. The precipitate was dried at 100°C for 5 hours. Morpho-structural changes were observed with increasing synthesis time and evaluated by chemical calculations. Electron microscopy has demonstrated that titanium oxide particles are obtained when a reaction time of up to 30 minutes is used, but a morphology change also occurs when a reaction time of 60 minutes is used when the formation of morphologies has been observed rod type. The anatase phase was obtained only after 1 min of reaction in addition to a small amount of brookite phase [47].

Table 6 presents the precursors, parameters and morpho-structural characterization

Table. 6 Morphology of titanium oxide, precursors, reaction parameters in microwave assisted method

Precursors	Hydrolysis agent	Parameters T(°C) t(h)	Morphology	Characterization method	Crystal Phase	BET m^2/g	Dim crystal
TIP	Propanol Ac-COOH HCl	400W 80°C	nanopowders Spherical,	SEM, XRD	A A+R+B	11-22	[45]
TIP	NaOH	5min		SEM, XRD, TEM	-	18-21	[46]
TIP	EtOH	120°C 200KPa		XRD, TEM	A	57-100	[47]

4. Conclusion

From the study of the specialized scientific works on the elaboration and characterization of titanium oxide and iron oxide with catalytic applications, important elements regarding: type of synthesis, methods of morpho-structural characterization, and methods of determining properties has been found. Based on the analysis regarding the researches performed on the synthesis and characterization of titanium oxide, the following conclusions were drawn:

- the stability of the different TiO_2 phases depends on the particle size, thus the anatase presents the most thermodynamically stable phase when the nanoparticles are smaller than 11 nm, and the rutile has been shown to be the most stable for the nanoparticles larger than 35 nm;
- the anatase phase of TiO_2 is known for its applications in photocatalysis, gas sensor, solar cells and electrochemical systems;
- the rutile phase of TiO_2 has applications in the construction of electric capacitors, filters, power circuits and capacitors due to its high dielectric constant;
- the structure dimension of TiO_2 has an impact on its properties and on the photocatalytic activity;
- so far, methods for the elaboration of titanium dioxide include chemical syntheses: hydrotermal, sol-gel, co-precipitation, sonochemistry, microwave assisted using a variety of precursors such as titanium alkoxides, titanium tetrachloride, titanium butoxide, titanium isopropoxide;
- the crystallite size of the titanium oxide nanoparticles elaborated by the hydrothermal method varies from 7.5 nm to 24nm;
- using the microwave assisted method, titanium oxide nanoparticles were developed whose crystallite size varies from 11 nm to 22 nm;
- the size of titanium oxide nanoparticles elaborated by the sonochemistry method varies from 15 nm to 38 nm;
- sol gel method obtained titanium oxide nanoparticles whose crystallite size varies from 23 nm to 40 nm;
- the size of the titanium oxide nanoparticles elaborated by the precipitation method varies from 4.5 nm to 47.3 nm;
- the characterization methods used for the morpho-structural characterization of titanium oxide are: SEM, XRD, TEM.

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